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RADIATION CHEMISTRY LABORATORY SERIES

RESEARCH REPORT NO. 4

IRRADIATION "FACTOR-DEPENDENCY"

Some Vinyl Monomers

Irradiation Cycle

XEROX

QUARTERMASTER RESEARCH & ENGINEERING CENTER

PIONEERING RESEARCH DIVISION

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FOREWORD

This is Research Report No. 4 of the Radiation Chemistry Laboratory Series on the general topic of Irradiation "Factor-Dependency." Some effects of parameters such as (1) dose, (2) dose rate, (3) irradiation cycle, and (4) temperature are reported for the irradiation-induced polymerization of nine monomer systems at three dose rates.

Research Report No. 1, Styrene, presented data indicating the significance of factors such as: (1) atmosphere, (2) degassing, (3) diluent, (4) dose, (5) dose rate, (6) moisture, and (7) temperature on irradiation-induced polymerization. A statistical study was included which vindicates the significance of atmosphere, dose rate, and temperature.

Research Report No. 2, Some Vinyl Monomers, included results giving evidence that under the conditions of these studies: (1) polymerization rate is not equal to $kI^{\frac{1}{2}}$, (2) the E-value (modified "G_e"-value) increases in general with a decrease in dose rate, (3) there is a non-additivity of dose, and (4) unless parameters are critically defined, the formulation of the rate of irradiation-induced polymerization of vinyl monomers has no apparent significance.

Research Report No. 3, Styrene With Additives, recorded results obtained from the irradiation-induced polymerization of styrene in the presence of eight additives. It was concluded that: (1) the effect of an additive is a function of dose rate with respect both to relative yield and to molecular weight of the polymer, (2) the molecular weight decreases in general with an increase in dose rate, regardless of the additive, (3) an additive which significantly increases the yield tends in general to produce somewhat lower molecular weight polymers, (4) an additive, as a function of dose rate, may either decrease or increase the yield of polymer, and (5) the efficiency of polymerization decreases markedly with the higher dose rates and dose levels.

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Irradiation "Factor-Dependency": Irradiation Cycle

By Ed. F. Degering, G. J. Caldarella, Flora E. Evans,
and Stephen Grib

A. Introduction

The experimental results reported herein represent relative rather than absolute values. This is a consequence of certain slight uncontrollable variations in parameters such as: (1) source of the monomer, (2) moisture content and other impurities, (3) uniformity of the flame-out of the tubes, (4) preparation of the samples, (5) wall thickness of the irradiation tubes, (6) fluctuation in the beam current and deviations in its distribution, (7) temperature, (8) refrigeration time between irradiation and processing, and (9) the processing procedure. To minimize experimental error, however, a meticulous routine procedure is used in the preparation, irradiation, and processing of the samples.

In the first exploratory studies by the Radiation Chemistry Laboratory, a shuttle which permitted a one to three-minute cycle and a conveyer with a twenty-minute cycle were both available. In spot experiments, there was an indication that the twenty-minute cycle is more efficient than the shuttle for the irradiation-induced polymerization of vinyl monomers. An experiment was planned, accordingly, for comparison of the yield of polymer obtained on a forty-five-minute cycle with the results from a three-minute cycle, a two-minute cycle, a one-minute cycle, and continuous irradiation. There was no significant difference, however, in the results from these three short cycles, hence the bar graphs give the average values obtained for the half-minute to three-minute cycles.

B. Preparation of Samples

In this particular study (D-682 to D-688) thirty samples were prepared for each of the monomer systems:
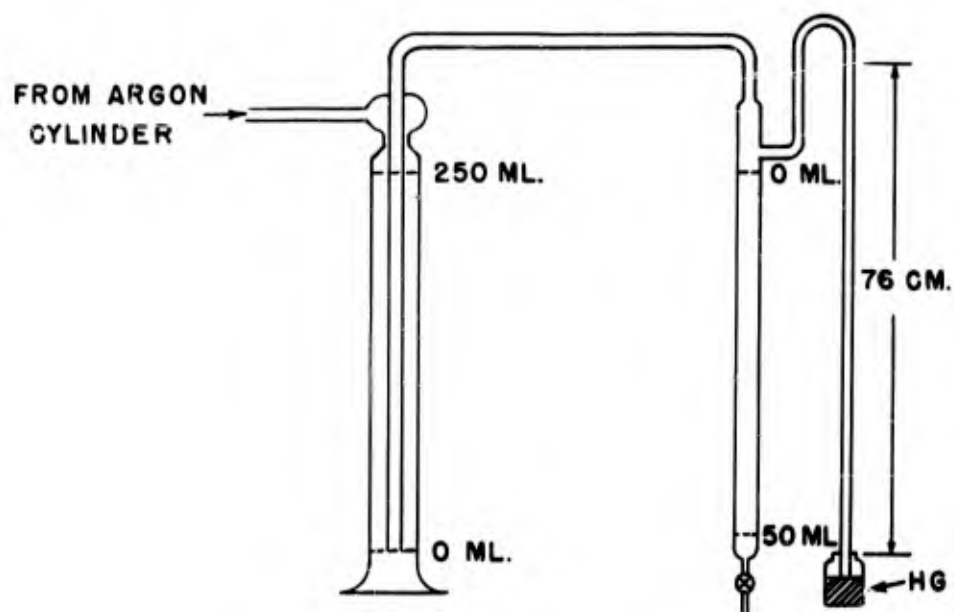
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Figure 1. Apparatus for measuring out samples of monomer in the presence of argon with slow flow of argon through the system to exclude both air and moisture.
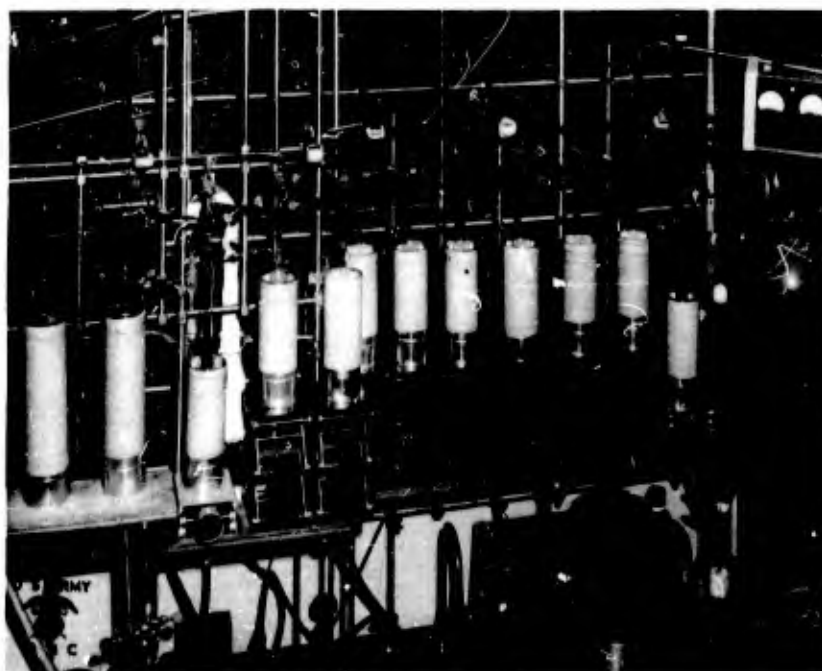

Figure 2. Apparatus used in preparation of samples.

acrylonitrile, butyl acrylate, styrene, vinyl acetate, acrylo-
nitrile-styrene (1/1 mixture by volume), butyl acrylate-styrene
(1/1), and vinyl acetate-styrene (1/1). Ten samples each of
1,1,3-trihydroperfluoropropyl acrylate and 1,1,7-trihydroper-
fluoroheptyl acrylate were also prepared (D-707).

The procedure developed in this laboratory for the
preparation of the monomer samples is as follows: The mono-
mer is vacuum distilled, dried several days in a refrigerator
over anhydrous potassium carbonate, and siphoned as used into
a 250 ml. glass-stoppered graduate, which is connected in turn
to an automatic burette through which a slow stream of argon
flows. The burette is filled from the graduate by use of slight
argon pressure (Figure 1, page 2).

Ten 1 × 12 inch pyrex test tubes, equipped with
ground glass male joints with a constriction in the tubing, are
placed on the vacuum manifold (Figure 2, page 2), flamed out
twice at 300 microns and once at 5 microns, and then filled with
argon. A 20 ml. portion of the desired monomer is transferred
from the burette to each of the argon-filled test tubes, which
are replaced in turn on the manifold. Then Dewar flasks of
liquid nitrogen are slowly raised by use of jacks in order to
freeze the monomer.[1] The stopcocks to the manifold are
opened one by one and the tubes evacuated to about 300 microns
by an auxiliary pump, which is connected to the right end of the
manifold (Figure 2, page 2).[2] The auxiliary pump is shut off
from the manifold, which is opened in turn to the high vacuum
system at the left. The pressure in the system is reduced to
five microns, the stopcocks given a one-fourth turn, the Dewar
flasks lowered, and the tubes sealed off and stored at -20°C

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(1) The level of the liquid nitrogen should be kept below the
     liquid-solid interface (except for the initial half-inch) until
     complete solidification has occurred in order to minimize
     breakage of the tubes.

(2) The auxiliary pump is used to avoid contamination of the
     high vacuum system, particularly in the case of a broken
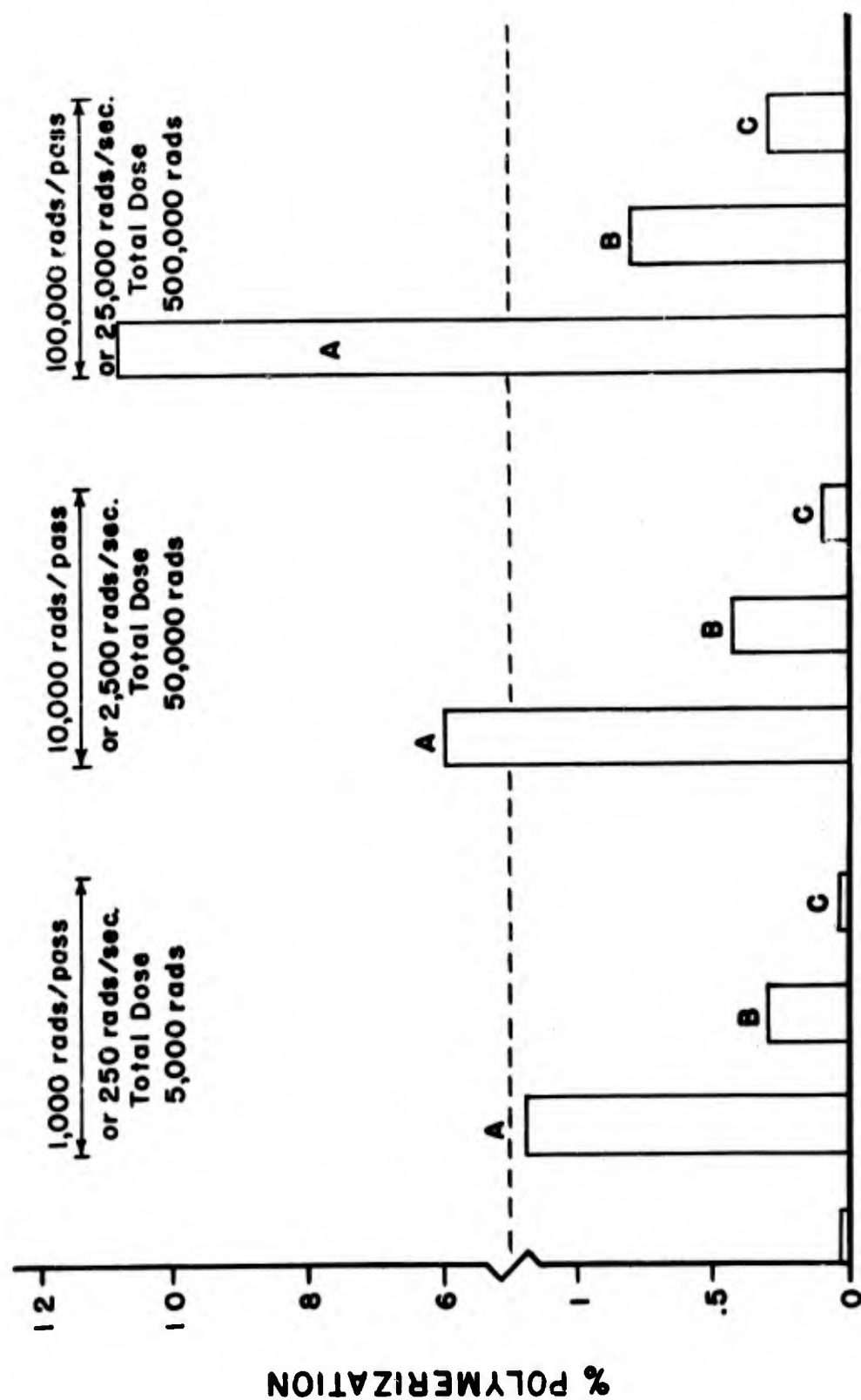   tube.

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Figure 3. Acrylonitrile (D-682): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. Comparable heat-control value indicated by bar at left.

% POLYMERIZATION

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until all of the samples are ready for packaging for irradiation. The tubes are then strip-packaged in polyethylene for convenience in handling, according to scheduled dose rate, and returned to storage at -20°C until time for irradiation.

C. Irradiation of Samples

Three irradiation procedures were employed in order to compare the technique developed by the Radiation Chemistry Laboratory (Procedure-1) with the two most commonly used with an electron accelerator (Procedure-2 and Procedure-3). Work is in progress with comparable samples on a forty-five-minute cycle at 25°C and limited studies have been initiated in which a gamma-source is used.

1. The samples were irradiated on a forty-five-minute cycle at 75°C, receiving five exposures at the dose rates indicated by the respective illustrations.

2. The samples were irradiated on a one-half-to three-minute cycle at room temperature, receiving five exposures at the dose rate given on the respective charts.

3. The samples were subjected to continuous irradiation at room temperature at the desired dose rate until the total exposure was equivalent to the five exposures received in Procedures-1 and -2.

The irradiation for the first two procedures was by use of a $1\frac{1}{2}$ Mev Van de Graaff electron accelerator (High Voltage Engineering Corporation), operating at 2 Mev, whereas the last procedure made use of a Resonant Transformer (General Electric Company) of 2 Mev capacity. The resonant transformer was used for the continuous irradiation because the Van de Graaff electron accelerator was not equipped to give continuous irradiation, but was very well adapted to the various time cycles employed in these studies. There is no thought here of a comparison of the two instruments per se. Variations from one instrument to the other are attributed to differences in the irradiation cycle.
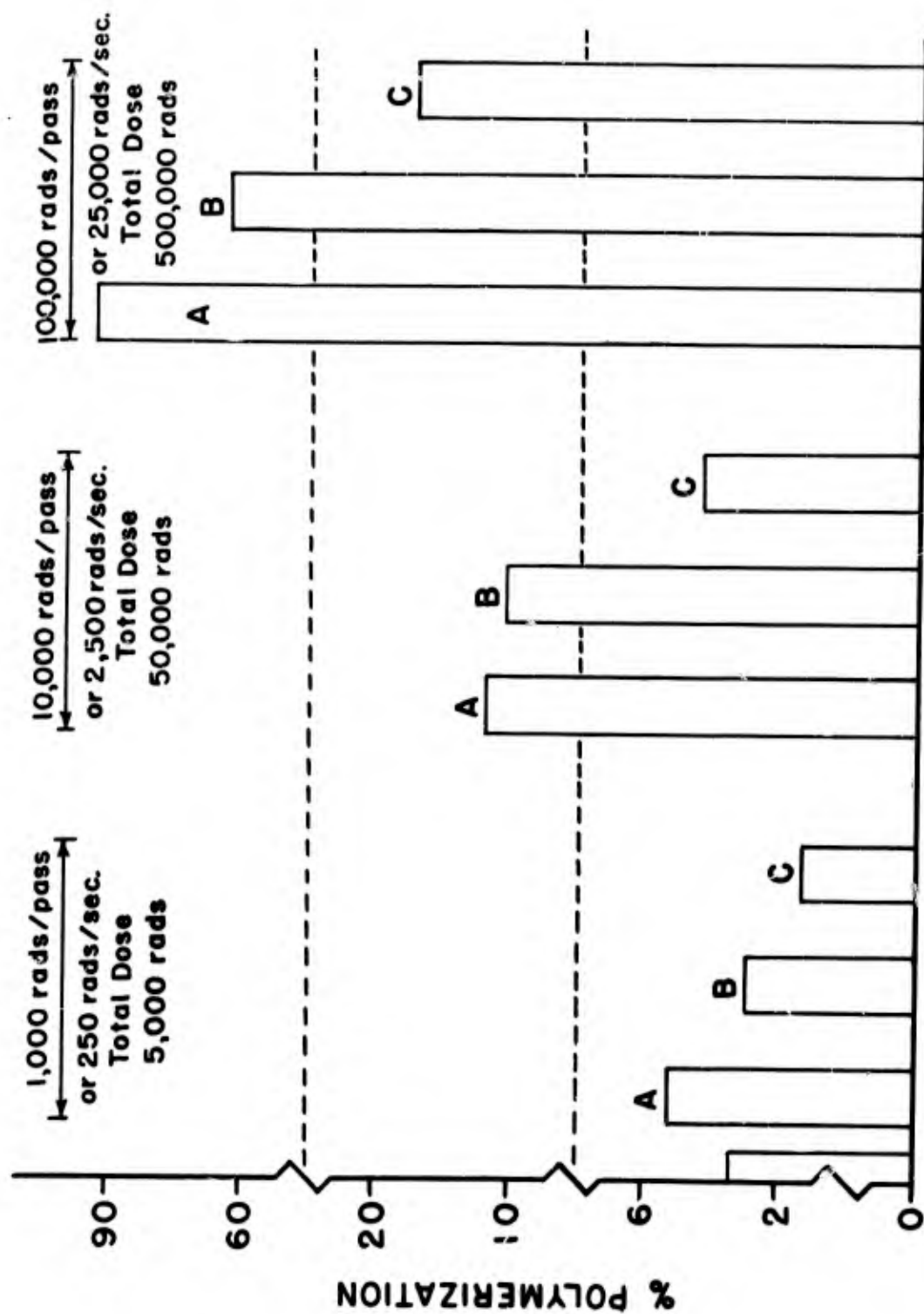
Figure 4. Butyl Acrylate (D-683): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. Comparable heat-control value indicated by bar at left. Samples for the A-bars received only one pass or a total of one-fifth of the irradiation received by the comparable samples for the B- and C-bars.

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The samples for Procedure-1 were placed according to scheduled dose rate in 1 × 1.5 foot aluminum trays, heated in a precision oven at 75°C for one-half hour, irradiated at the desired dose rate, returned to the oven for forty-five minutes, and then given comparable irradiation and heating until five cycles were completed. The aluminum trays were insulated from the conveyer by one inch of polystyrene foam.

After irradiation, the samples were returned to storage at -20°C until the tubes were opened for processing of the irradiated product.

D. Processing of Samples

The procedure developed for processing the irradiated monomer systems is as follows:

1. The tubes are scored on an emery wheel, cracked open with a hot glass rod. the contents transferred to the appropriate tared aluminum dish on a glass heating plate at about 60°C, the tubes rinsed well three times with methyl ethyl ketone, and the rinsings added to the respective aluminum dishes.

2. The contents of the aluminum dishes are evaporated to a residual film.

3. The aluminum dishes are placed in a vacuum oven at 85°C for four hours in order to remove residual monomer and solvent.

4. The aluminum dishes containing the polymer residues are conditioned in the balance room and weighed on a single-pan analytical balance.

5. The percent of polymerization is calculated from the known weight of 20 ml. of the monomer used and the weight of the polymer residue in the aluminum trays.
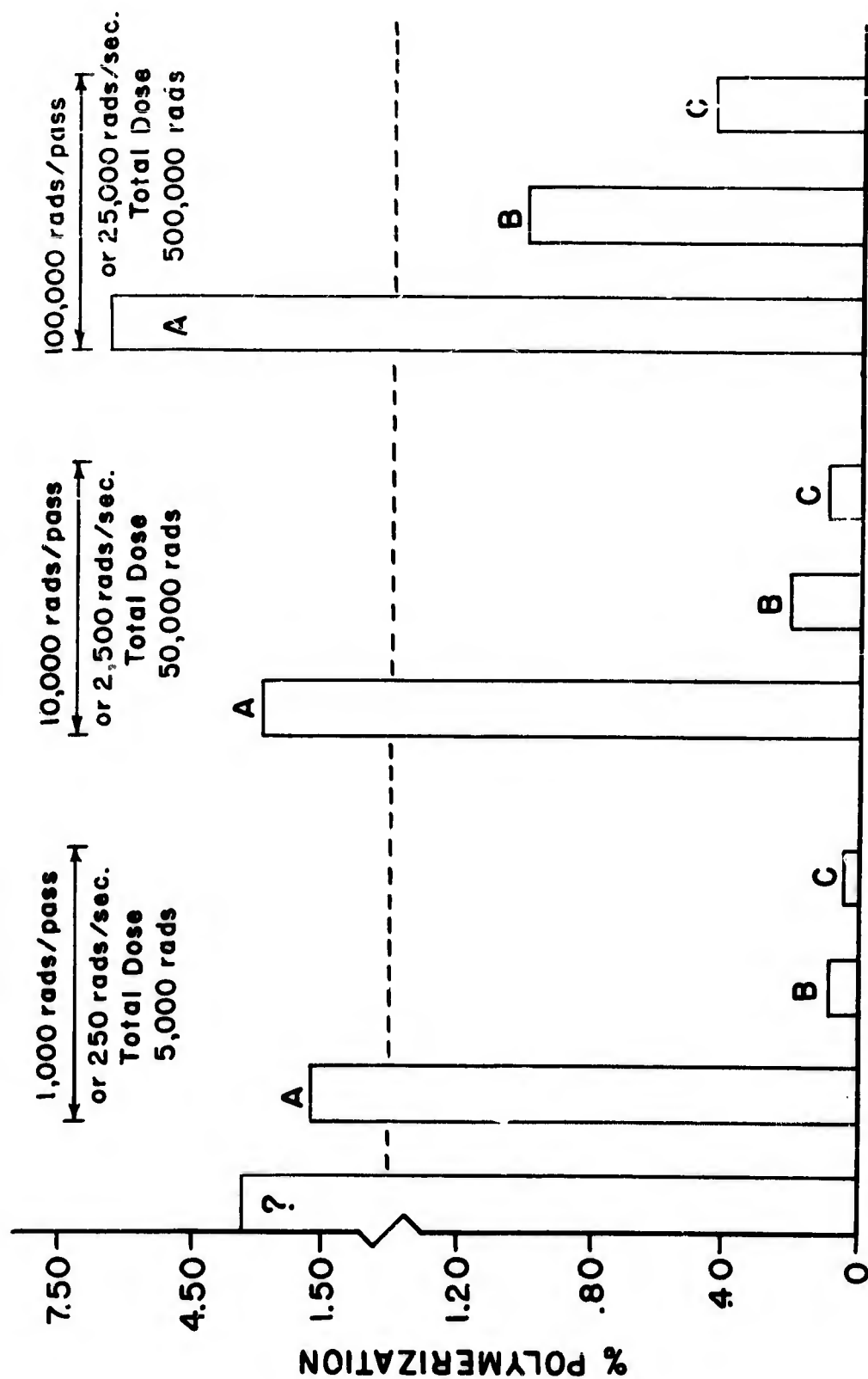
Figure 5. Styrene (D-684): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. Comparable heat-control value indicated by bar at left.

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6. To adjust for the variation in the wall thickness, the tubes are cut up and twenty micrometer readings recorded for each tube, in order to arrive at an average wall thickness. The average wall thickness is then multiplied by the density of the glass (2.23) to give a value from which the percent of ionization may be read directly from a graph (Res. Rpt. 3, Figure 41).[3] The percent polymerization, determined experimentally, is changed to an "adjusted value" by use of the formulation: "adjusted value" = (percent polymerization × 100)/(percent ionization), where it is assumed that, in the limited range of ionization involved (95 to 99%), the reaction rate is approximately linear with respect to dose rate. Adjusted values are believed to present better relative results.

E. Experimental Results

The bar graphs of the results obtained by the irradiation-induced polymerization of seven monomer systems by use of: (1) a forty-five-minute cycle at 75°C, (2) a half-minute to three-minute cycle at 25°C, and (3) continuous irradiation at 25°C are shown in Figures 3 to 9 (pages 4, 6, 8, 10, 12, 13, and 14), for dose rates of 250, 2,500, and 25,000 rads per second and corresponding doses of 5,000, 50,000, and 500,000 rads.

Results obtained are recorded graphically as: Figure 3, acrylonitrile (page 4); Figure 4, butyl acrylate (page 6); Figure 5, styrene (page 8); Figure 6, vinyl acetate (page 10); Figure 7, acrylonitrile-styrene (page 12); Figure 8, butyl acrylate-styrene (page 13); and Figure 9, vinyl acetate-styrene (page 14).

The A-bars in each graph are for the forty-five-minute cycles at 75°C, the B-bars in each graph are for the average values from the one-half-, one-, and three-minute cycles at 25°C, and the C-bars in each of these graphs are for continuous irradiation at 25°C. The comparable heat control
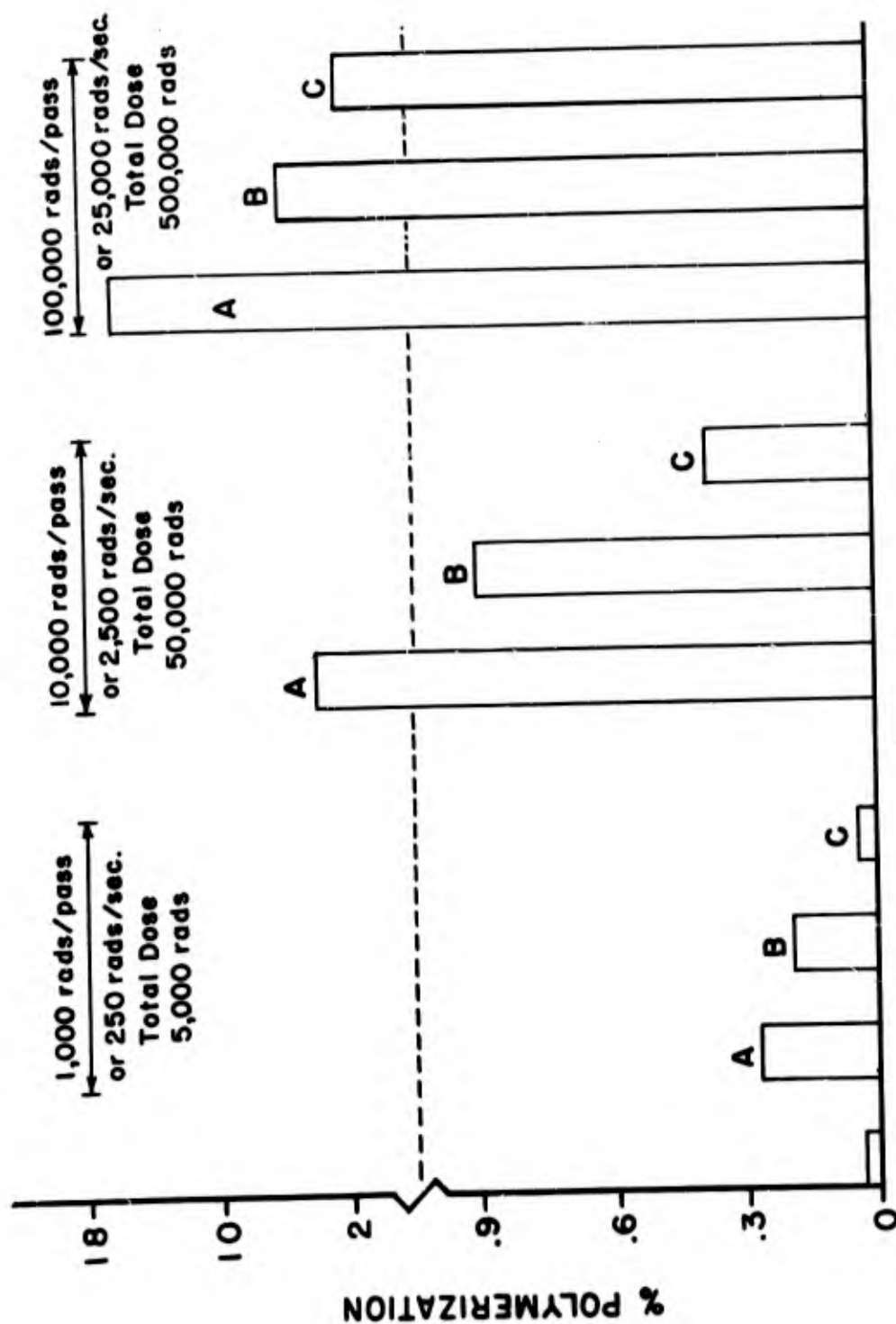
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(3) Trump, et al., J. App. Phys., 21, 346 (1950).

Figure 6. Vinyl Acetate (D-685): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. Comparable heat-control value indicated by bar at left.

samples on a forty-five-minute cycle at 75°C are shown in the lower left-hand corner of each of these bar graphs. The heat control bars of Figures 5, 7, and 8 are questionable. Abnormality in these, apparently a consequence of the monomer system, is unexplainable at the present. Further work is indicated.

It is apparent from the bar graphs of Figures 3 to 9 that the A-bars are significantly higher than are the B-bars, and that the B-bars in turn are significantly higher than are the C-bars. Stated otherwise, the highest yields of polymer are obtained by irradiation-induced polymerization on a forty-five-minute cycle at 75°C and the lowest yields are obtained consistently by the use of continuous irradiation. Other data obtained in this laboratory confirm this conclusion.

Values for the forty-five-minute cycle at 25°C are not yet available. It is not presumed, however, that either the forty-five-minute cycle or the temperature of 75°C are necessarily optimal for irradiation-induced polymerization of the monomer systems reported herein. Both the irradiation-time cycle and the temperature during the post-irradiation heating were selected as a matter of convenience. Determination of the optimum irradiation cycle and temperature, for each of these monomer systems, represents an extensive research study, which has not been undertaken to date in this laboratory.

The effectiveness of a relatively long irradiation cycle as compared to a relatively short cycle is believed to result from a fairly satisfactory balance of initiation, propagation, and termination in the polymerization process. In the shorter cycles the initiation and termination are doubtless dominating the reaction mechanism at the expense of propagation. This would result in much lower molecular weight products and, as a consequence of a superfluity of radicals, in many more decomposition products. Although both of these concepts may be explored experimentally, no studies along these lines have been undertaken to date in this laboratory.

From Figure 3 (page 4) it is observed that the forty-five-minute cycle for acrylonitrile is definitely better than the
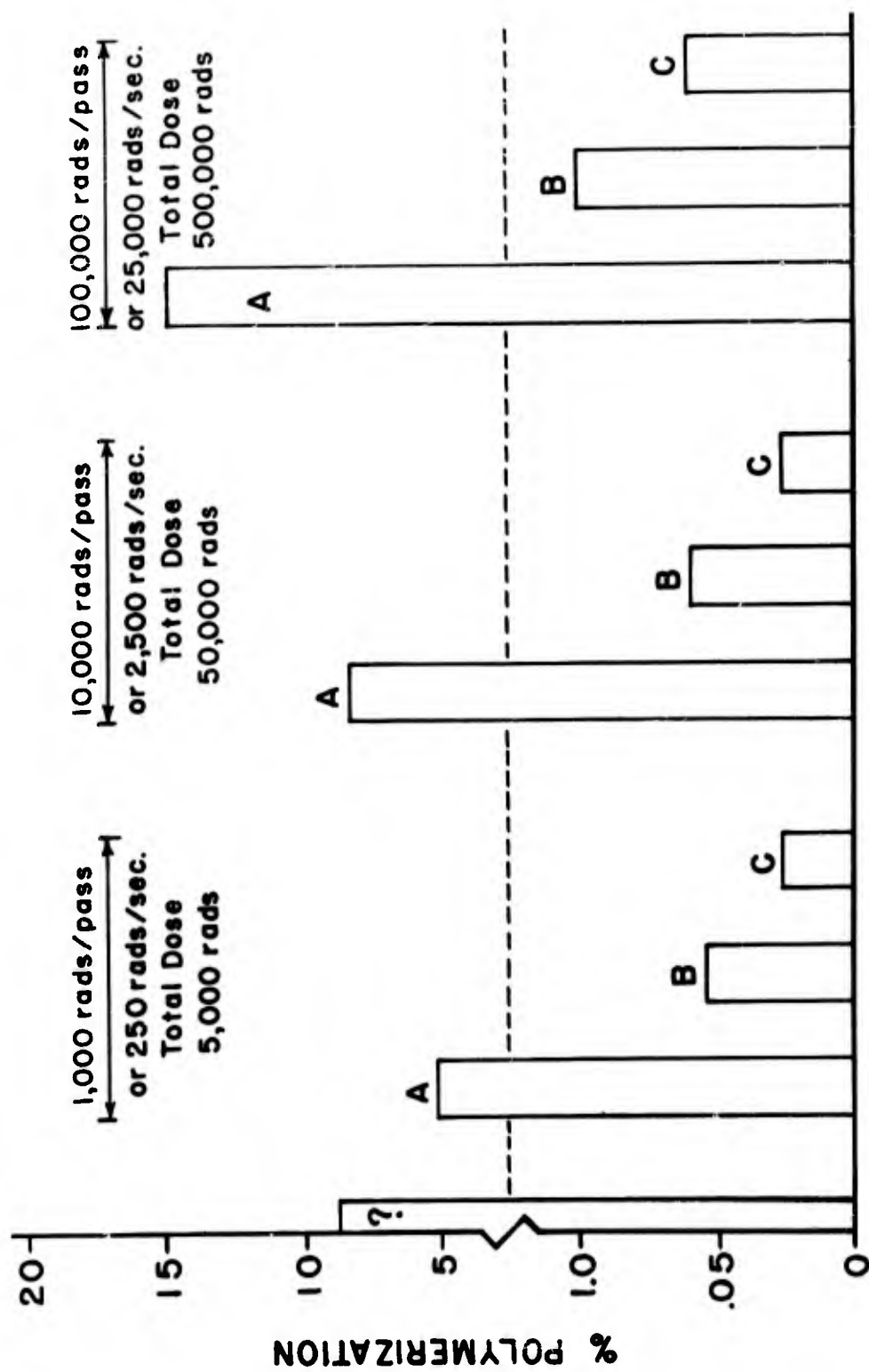
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Figure 7. Acrylonitrile-Styrene (1/1, D-686): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. Comparable heat-control value indicated by bar at left.

Figure 8. Butyl Acrylate-Styrene (1/1, D-687): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. Comparable heat-control value indicated by bar at left.

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Figure 9. Vinyl Acetate-Styrene (1/1, D-688): A. 45-minute cycle at 75°C, B. 1/2- to 3-minute cycle at 25°C, and C. continuous irradiation at 25°C. Comparable heat-control value indicated by bar at left.
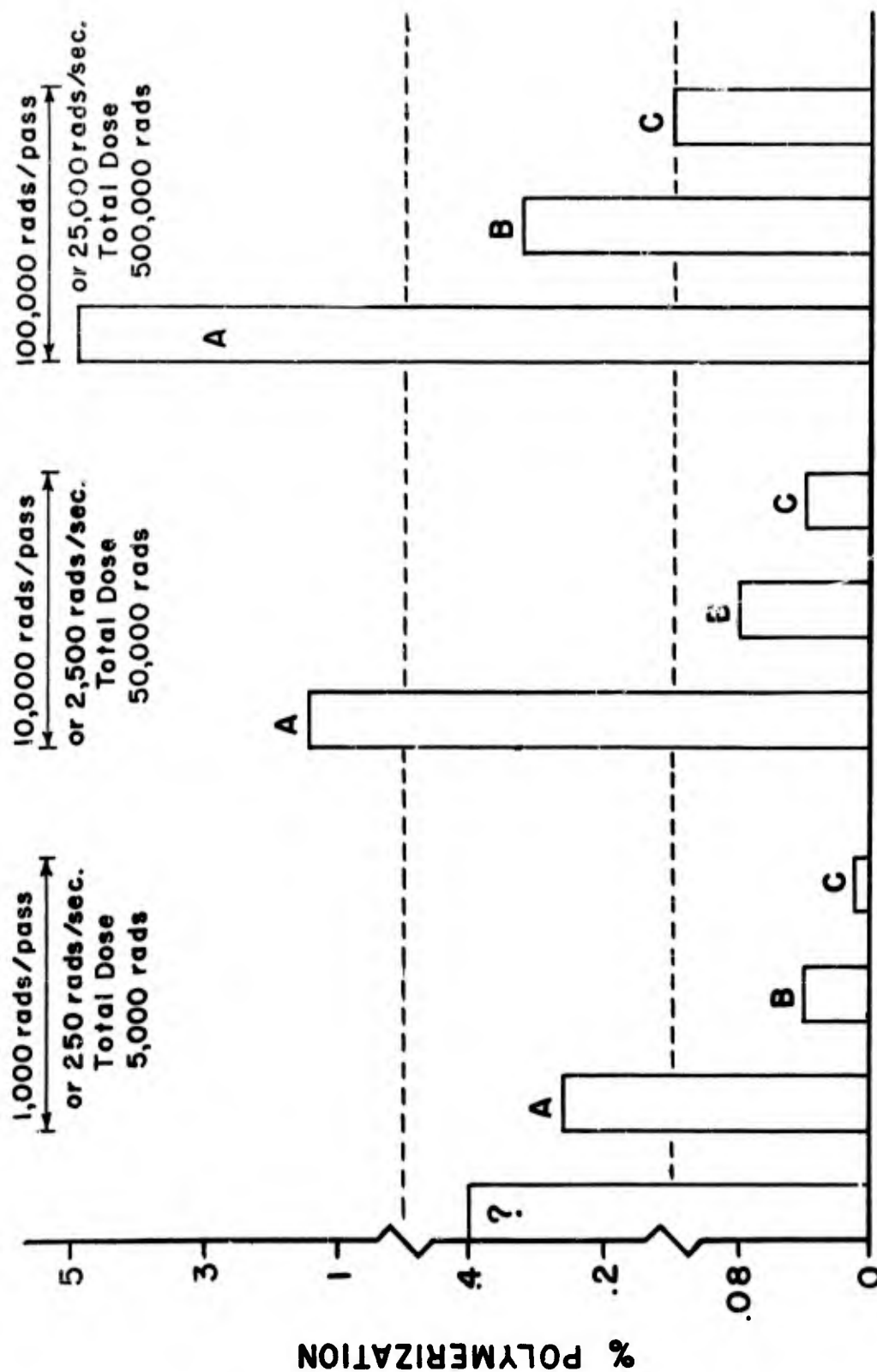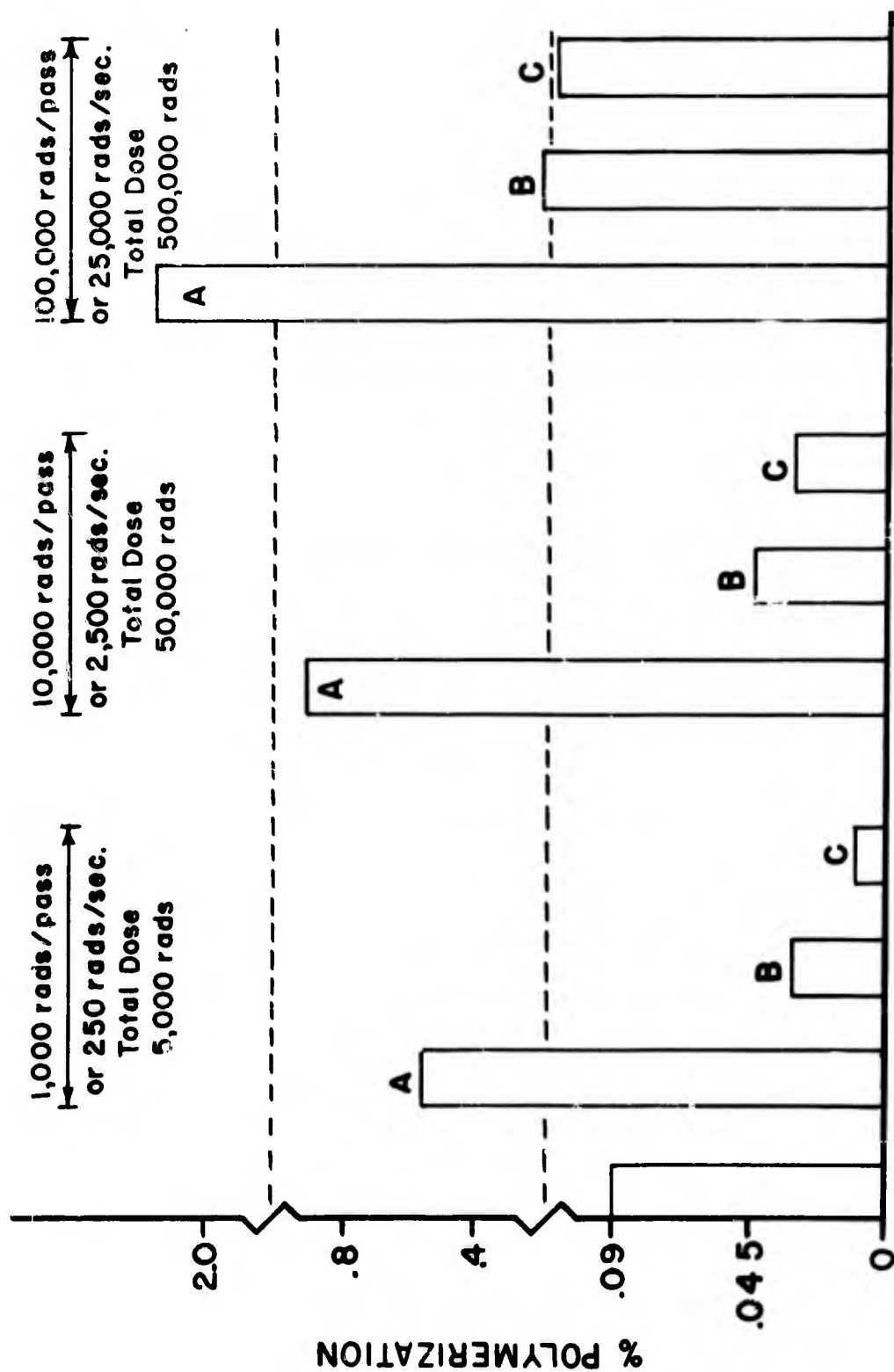
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one-half- to three-minute cycle at each of the three dose levels, and that the one-half- to three-minute cycle is better than is continuous irradiation. It is apparent, furthermore, from the heat-control bar in the lower left-hand corner that the heat effect represents the smallest value shown but there may be a synergistic effect when heat is combined with irradiation for the polymerization of monomer systems. It may be possible by an analysis of the accumulated data of this laboratory to determine (1) whether or not this apparent synergistic effect is real and (2) how it varies with the monomer system.

By a comparison of the A-bars for the three dose rates and three dose levels of Figures 3 to 9 (pages 4 to 14), it is apparent that the lowest dose rate (250 rads per second) is the most efficient and the highest dose rate (25,000 rads per second) the least efficient in these studies for the irradiation-induced polymerization of monomer systems. The formulations developed for reaction rate as a function of dose rate, moreover, derived under different experimental conditions, are not applicable to these systems under the experimental parameters of these studies.

Figures 10, 11, and 12 (pages 16, 18 and 20) summarize the results for the three irradiation procedures and the seven monomer systems by dose rate. The results obtained at 1,000 rads per exposure or 250 rads per second are given as Figure 10 (page 16), those at 10,000 rads per exposure or 2,500 rads per second as Figure 11 (page 18), and those at 100,000 rads per exposure or 25,000 rads per second as Figure 12 (page 20). The differences, in general, in the results obtained by Procedure-1 and Procedure-2 are the most pronounced for the acrylonitrile and the acrylonitrile-styrene systems, and least pronounced for the butyl acrylate and vinyl acetate systems. It is noted, moreover, that this difference varies with dose rate. This suggests that the most effective irradiation cycle is a function of both dose rate and the monomer system. The quotients for A-values divided by the C-values, A-values divided by the B-values, and B-values divided by the C-values are summarized in Table I (page 22). All quotients are greater than one.
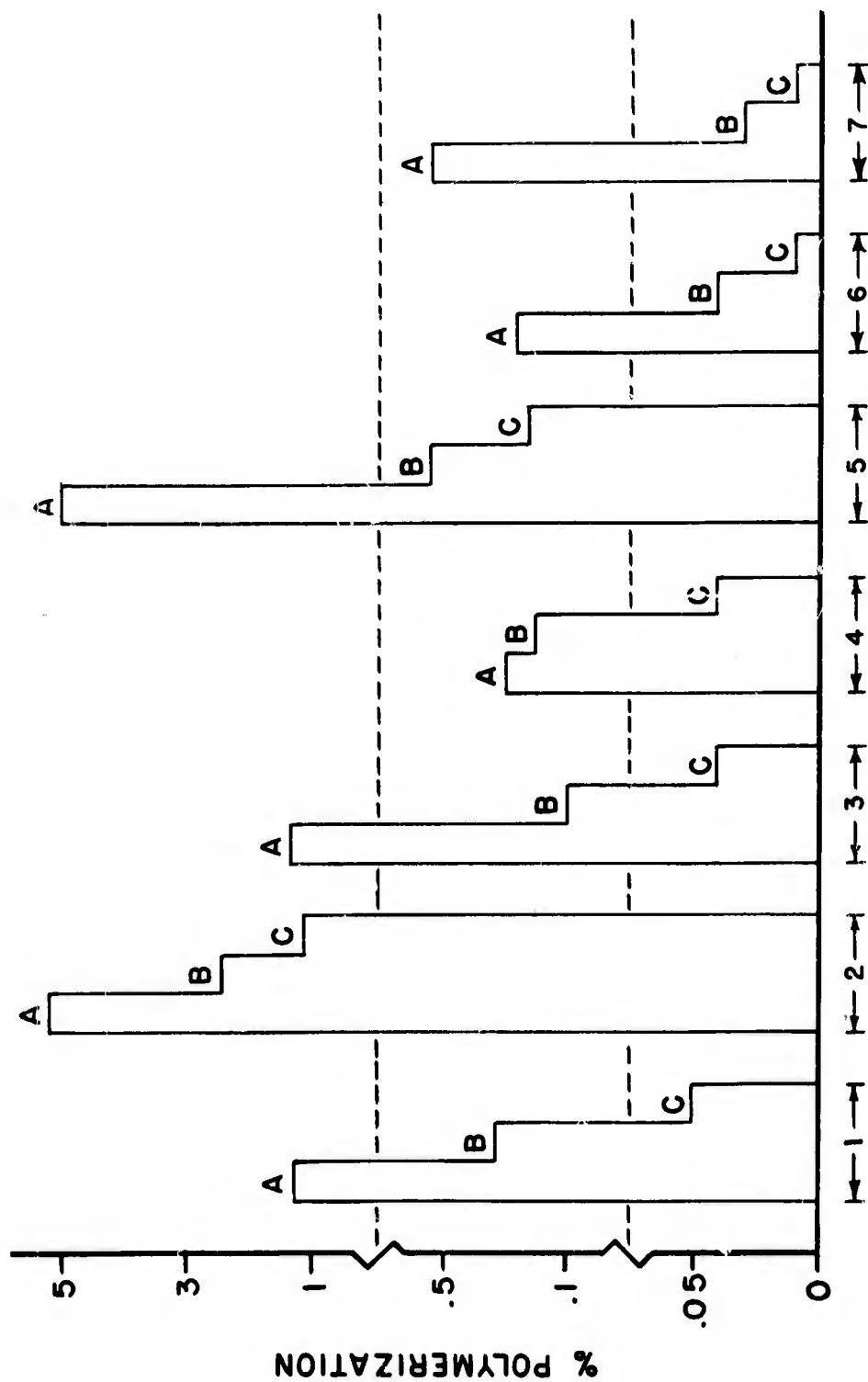
Figure 10. Monomers (D-682 to D-688), 1. Acrylonitrile; 2. Butyl Acrylate; 3. Styrene; 4. Vinyl Acetate; 5. Acrylonitrile-Styrene (1/1); 6. Butyl Acrylate-Styrene (1/1); 7. Vinyl Acetate-Styrene (1/1). Irradiation Cycle: A. 45-minutes at 75°C; B. 1/2 to 3 minutes at 25°C; C. continuous at 25°C. Dose Rate: 1,000 rads per exposure or 250 rads per second. Total Dose: 5,000 rads except butyl acrylate under the A group which had 1,000 rads only.

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The values indicated for butyl acrylate by the A-bars of Figures 4, 10, 11, and 12, however, cannot be compared directly with the corresponding B- and C-bars inasmuch as the samples for the latter had five times as much irradiation as did the samples for the corresponding A-bars. The quotients for A/C and A/B for butyl acrylate, consequently, are much higher for a comparable dose level than indicated in Table I (page 22).

Because of the availability of only limited amounts of 1,1,3-trihydroperfluoropropyl acrylate and 1,1,7-trihydroperfluoroheptyl acrylate, these samples were irradiated only by Procedure-1 and Procedure-3, that is, on a forty-five-minute cycle at 75°C and by continuous exposure at 25°C. The results are presented in the bar graphs of Figure 13 (page 21), for the three dose rates and dose levels. Each monomer had a dose of five times the indicated dose rate.

The general pattern that was noted relative to Figures 3 to 9 applies also to the two perfluoro monomers of Figure 13. Each of the A-bars represents data obtained from a forty-five-minute cycle at 75°C, whereas each of the C-bars presents the results obtained by continuous irradiation at the indicated rate until a total dose of 5,000, 50,000, or 500,000 rads were administered at the respective dose rates of 250, 2,500, or 25,000 rads per second.

The ratio of the A- to C-values for 1,1,3-trihydroperfluoropropyl acrylate at 250 rads per second is 6.49, at 2,500 rads per second it is 2.63, and at 25,000 rads per second it is 2.48.

The ratio of A- to C-values for 1,1,3-trihydroperfluoroheptyl acrylate at 250 rads per second is 8.2, at 2,500 rads per second it is 2.6, and at 25,000 rads per second it is 2.19.

The results for these two perfluoro acrylates are remarkably similar, and the difference between the results obtained by a forty-five-minute cycle at 75°C and those obtained by continuous irradiation decreases with an increase in dose rate.
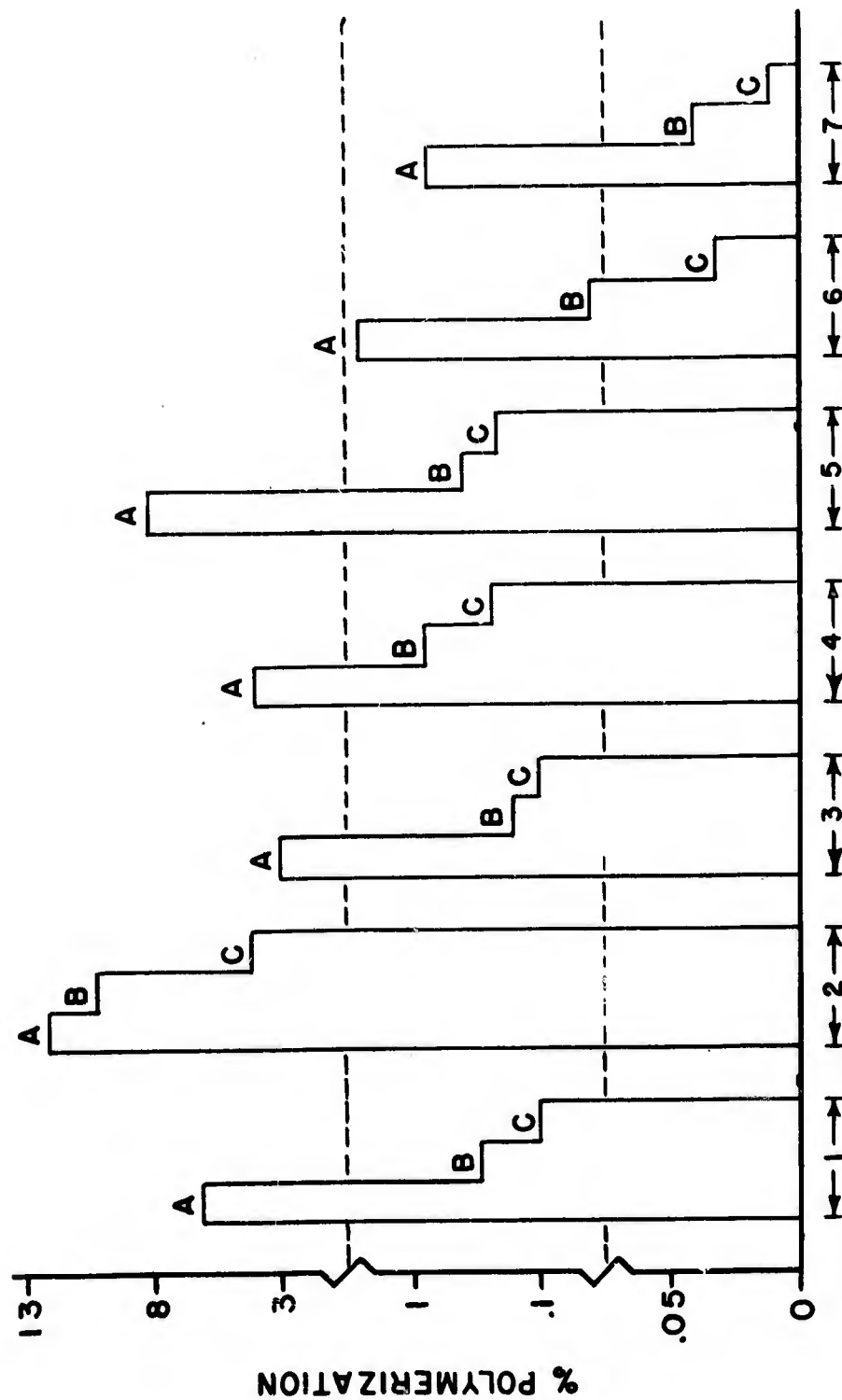
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Figure 11. Monomers (D-682 to D-688). 1. Acrylonitrile; 2. Butyl Acrylate; 3. Styrene; 4. Vinyl Acetate; 5. Acrylonitrile-Styrene (1/1); 6. Butyl Acrylate-Styrene (1/1); 7. Vinyl Acetate-Styrene (1/1). Irradiation Cycle: A. 45 minutes at 75°C; B. 1/2 to 3 minutes at 25°C; C. continuous at 25°C. Dose Rate: 10,000 rads per pass or 2,500 rads per second. Total dose: 50,000 rads except for butyl acrylate under the A group which received 10,000 rads only.

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F. Summary

From the results presented for the irradiation-induced polymerization of the nine monomer systems studied in this series, one may conclude that:

1. Something more than a three-minute cycle at 75°C (forty-five-minute cycle used as a convenient one in these studies) is the most efficient one for the irradiation-induced polymerization of the systems studied.

2. The efficiency of polymerization on a given time cycle, as noted in previous reports, decreases markedly for the higher dose rates used in this study.

3. The relative efficiency of polymerization on a time cycle compared with continuous irradiation appears to decrease with an increase in dose rate.

4. The reaction rate formulations for these systems, derived under vastly different experimental conditions, are not applicable to the parameters used in this study.

5. The most desirable time cycle and temperature depend on the nature of the monomer system.
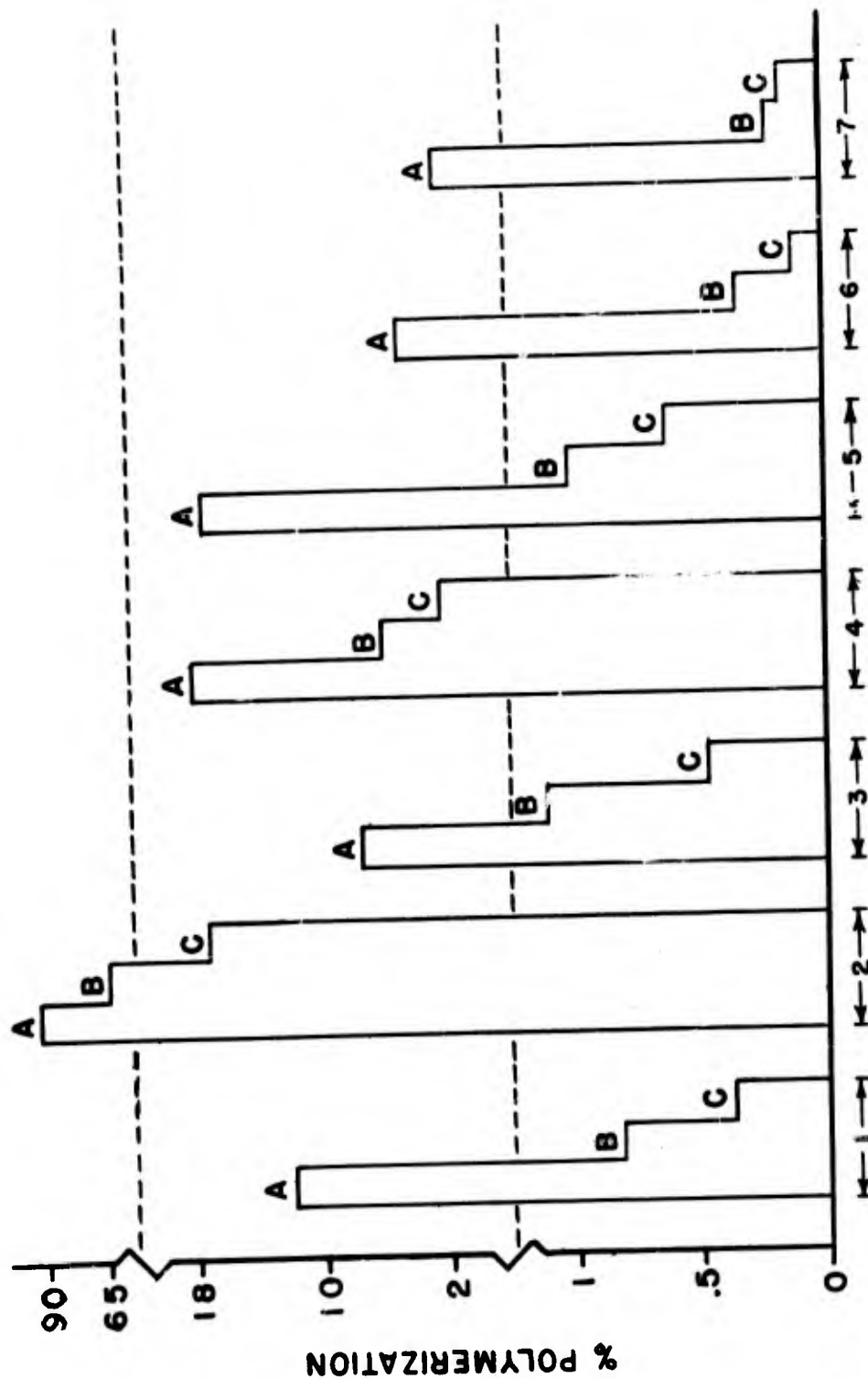
G. Acknowledgements

Figure 12. Monomers (D-682 to D-688), 1. Acrylonitrile; 2. Butyl Acrylate; 3. Styrene; 4. Vinyl Acetate; 5. Acrylonitrile-Styrene (1/1); 6. Butyl Acrylate-Styrene (1/1); 7. Vinyl Acetate-Styrene (1/1). Irradiation Cycle: A. 45-minute cycle at 75°C; B. 1/2- to 3-minute cycle at 25°C; C. continuous at 25°C. Dose Rate: 100,000 rads per pass or 25,000 rads per second. Total Dose: 500,000 rads except for butyl acrylate under the A group which received 100,000 rads only.
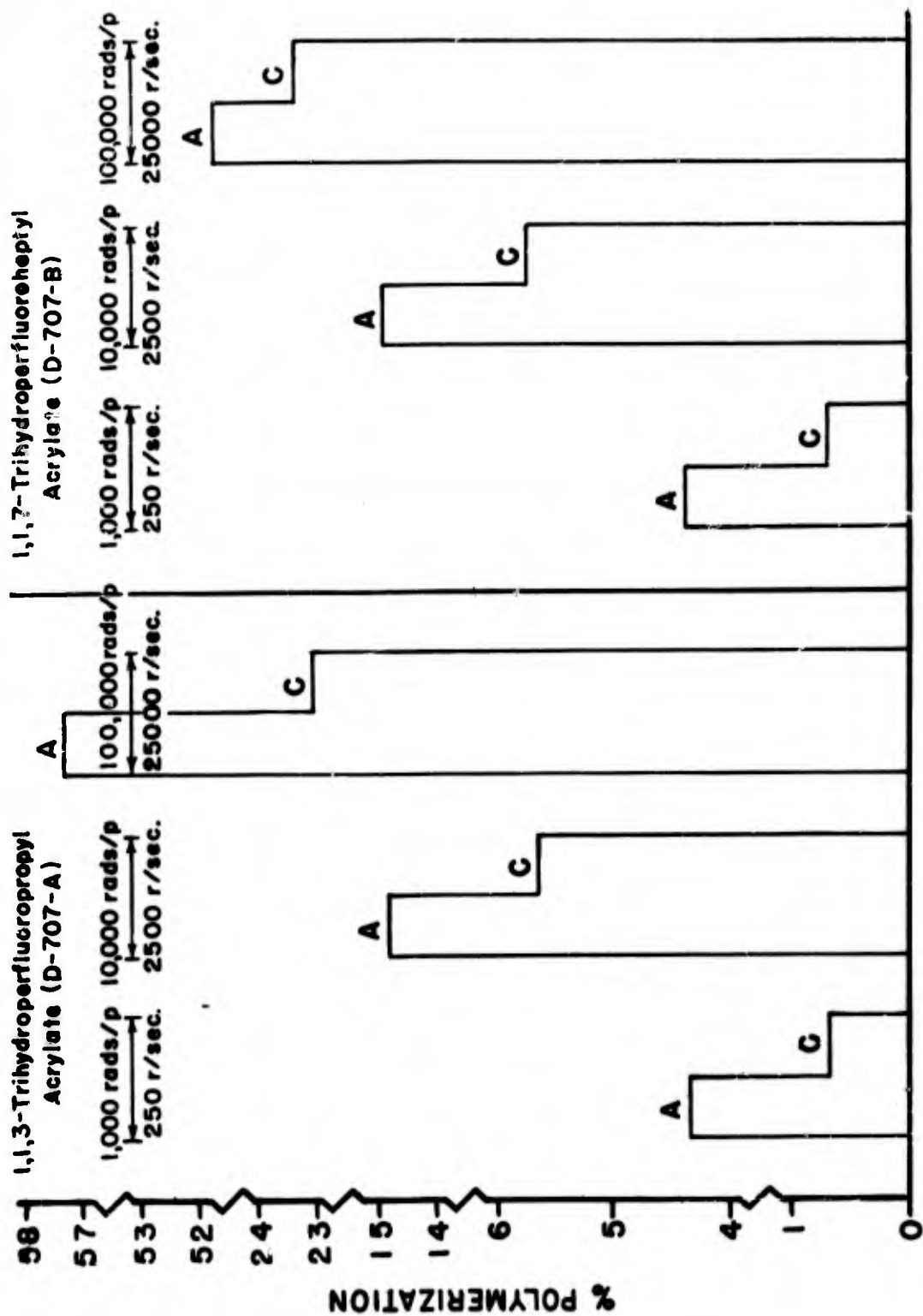
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Figure 13. Left, 1,1,3-trihydroperfluoropropyl acrylate; Right, 1,1,7-trihydroperfluoro-heptyl acrylate (D-707): A. 45-minute cycle at 75°C, and C. continuous irradiation at 25°C. Corresponding heat control values are 0.006 and 0.004.

TABLE I

Quotients from Figures 10, 11, and 12 for A/C, A/B, B/C

Monomer System	At 1,000 r/p or 250 r/sec.			At 10,000 r/p or 2,500 r/sec.			At 100,000 r/p or 25,000 r/sec.		
	A/C	A/B	B/C	A/C	A/B	B/C	A/C	A/B	B/C
1. Acrylonitrile	24.8	3.9	6.4	63.0	13.7	4.6	33.9	15.1	2.3
2. Butyl Acrylate	3.9	1.8	2.2	2.8	1.2	2.4	5.4	1.5	3.6
3. Styrene	44.0	19.6	2.3	30.0	14.3	2.0	16.6	6.8	2.4
4. Vinyl Acetate	7.0	1.4	5.0	10.6	4.4	2.4	7.8	3.0	2.6
5. Acrylonitrile-Styrene (1/1)	22.8	9.1	2.5	27.3	14.1	1.9	28.7	17.7	1.6
6. Butyl Acrylate-Styrene (1/1)	26.0	6.5	4.0	47.0	17.6	2.7	44.3	15.2	2.9
7. Vinyl Acetate-Styrene (1/1)	55.0	18.3	3.0	91.0	22.8	4.0	14.4	11.0	1.3

NOTES: The A-values are from the forty-five-minute cycle at 75°C, the B-values are the average for a one-half-, one-, and three-minute cycle at 25°C, and the C-values are for continuous irradiation.

The total doses involved are, left to right, 5,000, 50,000, and 500,000 rads.

These quotients are all greater than 1. The A/C-values at 250 rads per second are all greater than 3.9, at 2,500 rads per second they are all greater than 2.8, and at 25,000 rads per second they are all greater than 5.4, for these seven monomer systems. The highest quotient obtained is for vinyl acetate at 10,000 rads per second, where the value is 91.0, or the polymerization is 91 times more efficient by Procedure-1 than by Procedure-3.

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